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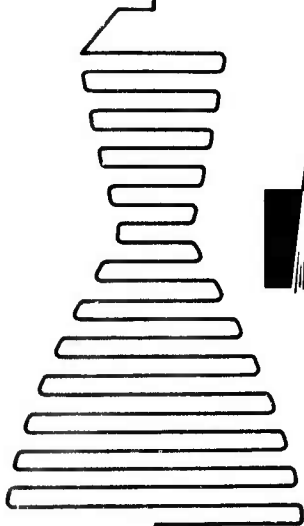
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INORGANIC HALOGEN OXIDIZERS

(1 December 1964 through 28 February 1965)

Group 4
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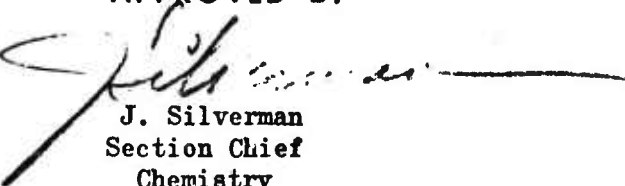
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FOREWORD

The research reported herein was supported by the Advanced Research Projects Agency and was monitored by the Office of Naval Research, Power Branch, Code 429, Washington 25, D.C., with Mr. Richard L. Hanson as Scientific Officer. This report was prepared under Rocketdyne G.O. 8614 in compliance with Section H of Contract Nonr 4428(00) under ARPA Order No. 23, and covers the period 1 December 1964 through 28 February 1965.

The Responsible Scientist for this program is Dr. D. Pilipovich, Principal Scientist, Fluorine Chemistry Unit, with Dr. H. F. Bauer, Dr. C. J. Schack, and Mr. R. D. Wilson serving as full-time associates. The work was carried out in the Synthetic Chemistry Group under the direction of Dr. E. A. Lawton, Group Scientist.

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ABSTRACT

The synthesis of F_3ClO was attempted by reactions of ClF_5 with yellow mercuric oxide and systems involving potassium nitrate and perchlorate. No evidence of F_3ClO was found, even as an intermediate. The reaction of ClF_3 and O_3 gave $FClO_2$, ClO_2 , and unidentified compounds with infrared bands at 5.1, 8.7, and 12.9 microns.

Calcium hypochlorite and chlorine monoxide were fluorinated under a variety of conditions. At $-80^\circ C$ in the presence of CsF , Cl_2O reacted with F_2 to give an unidentified compound which may be a new $Cl-F-O$ species.

The dissociation of the complex $NF_2O^+BF_3Cl^-$ was examined in the hope of producing $ClNF_2O$. The only chlorine-containing product found was Cl_2 .

Fluorine nitrate and the potassium fluoride-difluorine complex were reacted in the hope of forming NF_2ONO_2 . The products were N_2F_4 , NO_2 , and FNO_2 , suggesting the initial formation of NO_3^\cdot and NF_2^\cdot radicals.

The fluorination of BrF_5 at low temperatures was attempted by electrical discharge techniques. No new BrF species were indicated.

In an effort to synthesize NF_2 -substituted interhalogen compounds, chlorine trifluoride, chlorine pentafluoride, and

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iodine pentafluoride were reacted with difluoramine. Various complexes of both ClF_3 and HNF_2 were explored as well. The major product was ClNF_2 (as high as 95 percent), and the absence of Cl_2 and ClF strongly suggested NF_2ClF_2 as an intermediate. Inability to isolate NF_2ClF_2 was attributed to an enhanced reactivity of the Cl-F bonds toward HNF_2 . The relative reactivities for the systems examined were: $\text{ClF}_3\text{-HNF}_2 > \text{ClF}_5\text{-HNF}_2 > \text{ClF}_3\text{-HNF}_2\text{:BF}_3 > \text{ClF}_2^+\text{BF}_4^-\text{-HNF}_2 > \text{RbClF}_4\text{-HNF}_2 \sim \text{KF-KClF}_4\text{-HNF}_2$. Difluoramine reactions with IF_5 resulted in degradation products which included I_2 .

The synthesis of NF_2ClO_2 was attempted by reacting HNF_2 with FClO_2 as well as its BF_3 complexes. In the absence of BF_3 , deflagrations occurred, probably due to ClO_2 impurities. In the presence of BF_3 , the principal nitrogen-containing product was NOBF_4 .

(Confidential Abstract)

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INTRODUCTION

This report is the third quarterly progress report on a program directed toward the preparation of new inorganic oxidizers. Of particular interest are new oxyhalogen fluorides, oxynitrogen fluorides, and difluoramino-substituted interhalogens and oxyhalogen fluorides. Metathetical reactions and routes involving the formation of radical intermediates are being explored to this end. Low-temperature catalytic fluorinations also are being employed. In the previous report periods, fluorination by discharge-excited fluorine was used, but no new stable compounds were formed. Metathetical reactions of ClF_5 with several oxygen sources had also proved unsuccessful. Difluoramine reactions with interhalogens began during the second quarter and constitute a major portion of the current effort.

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DISCUSSION

Recent attention has been given to the synthesis of FClO , F_3ClO , and $\text{F}_2\text{N-ClF}_2$. Efforts have also been made toward the fluorination of BrF_5 and the formation of new NF_2O compounds.

ATTEMPTED SYNTHESIS OF F_3ClO

Metathetical Reactions

Various metathetical reactions of ClF_5 with oxygen sources have been attempted in the hope of producing F_3ClO (Ref. 1). Although these routes to F_3ClO have not been successful, mercuric oxide appeared to be a promising oxygen source (Ref. 1) for a controlled Cl-O bond formation under mild conditions. A slow stream of ClF_5 , diluted by N_2 , was passed through a Kel-F U-tube packed with HgO on copper shot at 0 C. No new products were identified.

Since a straightforward substitution of an oxygen atom for two fluorine atoms has not been fruitful to date, it was hoped to form F_3ClO through decomposition of the hypothetical species F_4ClONO_2 or $\text{F}_4\text{ClOClO}_3$. Should F_3ClO disproportionate to ClF_5 and FClO_2 , it was hoped that these reactions would at least provide some evidence of disproportionation.

The reaction of $\text{ClF}_4^+\text{AsF}_6^-$ with KNO_3 yielded only ClF_5 and solids which did not contain chlorine. Hydrogen fluoride was added to increase low-temperature contact and favor KF formation. In the presence of stoichiometric amounts of HF , the products were ClO_2 , FClO_2 , FClO_3 , and

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solids, presumably KHF_2 and $\text{NO}_2^+\text{AsF}_6^-$. Elimination of AsF_5 as a reactant gave similar results except that FNO_2 was observed. The addition of HF probably changed the reactant KNO_3 to HONO_2 , thus promoting the observed reactions. The presence of large amounts of ClO_2 and FClO_3 indicated that ClF_5 reacted with a hydroxy compound (Ref. 2). The decomposition of F_4ClONO_2 to F_3ClO might have been followed by disproportionation to ClF_5 and FClO_2 but not to large amounts of FClO_3 .

The reaction of ClF_5 and KClO_4 with HF added was not expected to involve a hydroxy compound exclusively, since HOClO_3 is a stronger acid than HF. Although no reaction was noted at 150 C for prolonged periods in the absence of HF, a stoichiometric amount of H₂ caused ClO_2 , FClO_2 , and FClO_3 to be formed. Even the application of conditions sufficient for incipient reaction gave identical products, suggesting that the fluorination of ClO_4^- to give oxygen is the only reaction. Again, no evidence for F_3ClO , even as an intermediate, was obtained.

Oxidation Reactions

Another route to F_3ClO under consideration is the combination of ClF_3 and atomic oxygen. The reaction of SF_4 and a mixture of NO_2 and O_2 under ultraviolet light is known to give F_4SO (Ref. 3). The reaction of ClF_3 and O_3 was intended to produce F_3ClO . A 2:1 O_3 - ClF_3 mixture was condensed into a Kel-F infrared gas cell at -196 C and allowed to warm to room temperature while scanning. Although Pennsalt (Ref. 4) has found no products from bubbling O_3 through ClF_3 , a short-lived product could have escaped detection in a flow reaction where products are examined later

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By following infrared absorbances as a function of time, the rate of ozone decomposition was found to be apparently dependent on ozone concentration, in agreement with the results of Benson and Axworthy (Ref. 5), whereas the reaction of ClF_3 to FClO_2 proceeded at a constant, slow rate. Ultraviolet irradiation of the mixture had no marked effect on these rates and may have been of insufficient power to penetrate the Kel-F cell body. Although no infrared bands definitely attributable to FClO or F_3ClO were found, unidentified bands at 5.1, 8.7, and 12.9 microns appeared and increased during the course of the reaction. Further study on this reaction is planned.

FLUORINATION OF Cl-O COMPOUNDS

The synthesis of new F-Cl-O compounds has been attempted previously by fluorination of compounds containing Cl-O bonds. Low-temperature reaction of FClO_2 with excited fluorine yielded no new stable products (Ref. 1). Since compounds with only one Cl-O bond should provide a more facile route to compounds such as FClO , F_3ClO , and F_5ClO , the fluorination of calcium hypochlorite and chlorine monoxide has been examined.

Calcium Hypochlorite

Excess fluorine and calcium hypochlorite reacted at 125 C in a stainless-steel cylinder to form FClO_3 . The same reaction at room temperature produced FClO_3 , FClO_2 , and a trace of Cl_2O_6 as volatiles. When the hypochlorite was mixed with dried, powdered CsF and reacted with fluorine at -80 C, the gas products were FClO_3 , FClO_2 , ClO_2 , and a trace of SO_2F_2 . Bunn (Ref. 6) has stated that the X-ray examination of calcium hypochlorite

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indicates that the composition is $3 \text{ Ca}(\text{OCl})_2$, $2 \text{ Ca}(\text{OH})_2$, $2 \text{ H}_2\text{O}$ and $\text{Ca}(\text{OCl})_2$, $2 \text{ Ca}(\text{OH})_2$. Apparently, fluorination of the OH groups occurred in preference to the formation of new F-Cl-O species.

Chlorine Monoxide

A greater chance for success was anticipated in the fluorination of Cl_2O since oxygen is bonded only to chlorine. When Cl_2O and F_2 were reacted in a stainless-steel cylinder at 125 C, ClF_3 , FClO_2 , and ClO_2 resulted. By condensing Cl_2O over dried CsF at -80 C and reacting with fluorine, FClO_2 and ClO_2 were obtained in addition to an unidentified compound. Infrared absorptions in the Cl-O and Cl-F regions support a chlorine oxyfluoride candidate. This last experiment is being repeated in an attempt to produce sufficient quantities of the unknown for identification.

REACTIONS LEADING TO NEW NF_2O COMPOUNDS

Attempted Synthesis of ClNF_2O

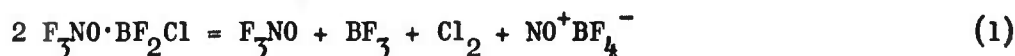
The existence of ClNF_2 and F_3NO suggested the possibility that ClNF_2O may exist as well. The likely approach to the synthesis of this molecule was by the dissociation of the complex $\text{NF}_2\text{O}^+\text{BF}_3\text{Cl}^-$, where the dissociation products would be F_3NO , BF_2Cl , and possibly some ClNF_2O and BF_3 . Since BF_2Cl readily establishes an equilibrium with BF_3 , BFCl_2 , and BCl_3 at room temperature (Ref. 7), a 5:1 BF_3 - BCl_3 mixture was allowed to equilibrate; it was then frozen, and the excess BF_3 was pumped off at -142 C. The residual mixture, rich in BF_2Cl , was reacted with F_3NO at -142 C and allowed to warm to -80 C. Further warming resulted in the formation of

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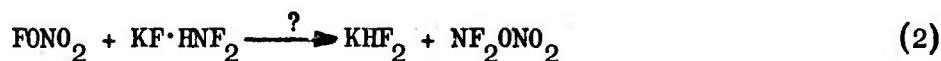
Cl_2 , F_3NO , BF_3 , and a white solid, probably NO^+BF_4^- . The reaction written on the basis of the recovered products is:



Whether chlorine resulted from BF_2Cl oxidation or ClNF_2O instability is not known.

Attempted Synthesis of NF_2ONO_2

In an effort to extend the synthesis of ONF_2 compounds to inorganic chemistry, a method recently discovered at Rocketdyne with organic hypofluorites under Contract AF04(611)-9377 was applied to fluorine nitrate, an inorganic OF compound. Fluorine nitrate was reacted with the potassium fluoride-difluoramine complex in an attempt to produce NF_2ONO_2 :



The experiment was conducted in a Kel-F ampoule and kept at -80°C for approximately 40 hours. Examination of the gaseous products after fractionation revealed the presence of only NO_2 , FNO_2 , and N_2F_4 . None of the desired product was obtained. However, it is interesting to note that N_2F_2 , NF_3 , FNO , and F_3NO were absent as well. The results are consistent with the initial production of NO_3^\cdot and NF_2^\cdot radicals. Since N_2F_2 was not a product, the formation of HF was probably due to the reaction of FONO_2 with HNF_2 rather than the decomposition of the $\text{KF} \cdot \text{HNF}_2$ complex. The instability of the resultant NO_3^\cdot radical could then explain

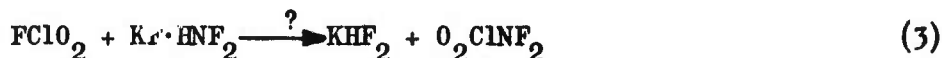
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the failure to achieve the desired NF_2ONO_2 . A more stable radical such as $\text{ClO}_2\cdot$ may allow the formation of the compound O_2ClNF_2 :



Studies on this reaction are in progress.

FLUORINATION OF BrF_5

The synthesis of BrF_7 had been attempted previously at Rocketdyne by the fluorination of CsBrF_6 as well as BrF_5 itself. Failure to obtain BrF_7 may have been due to its instability with respect to BrF_5 and F_2 except at low temperatures. Therefore, the reaction of BrF_5 , frozen at -196°C , with a discharge-excited fluorine stream was attempted. When the frozen products were slowly warmed, no noncondensibles were observed, in contrast to similar fluorinations of N_2O_4 and FCIO_2 (Ref. 1). Similar negative results were obtained when a stream of premixed BrF_5 and excess F_2 was passed through a glow discharge and immediately frozen. The only Br-F compound found was the starting material.

METATHETICAL REACTIONS OF HNF_2

During this period a thorough investigation of the reactions between Cl-F compounds and difluoramine was initiated and is continuing.

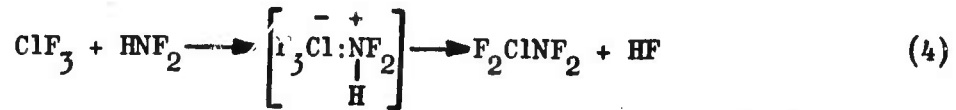
The reactions of Cl-F compounds and difluoramine were undertaken as a possible method for producing new derivatives of interhalogen fluorides. Specifically, it was proposed (Ref. 8) that the low-temperature reaction of ClF_3 and HNF_2 might lead to the coordination of these two materials and the formation of a Cl-N bond followed by the elimination of HF.

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in this manner an NF_2 -substituted interhalogen might be synthesized.

Apparatus Reactivity

Initial efforts were conducted in a metal-Teflon vacuum system. However, it was soon determined that the decomposition of HNF_2 on the fluorine-treated metal surfaces occurred too rapidly to allow effective mixing of the reactants for reasonable time periods. This decomposition reaction resulted in the conversion of HNF_2 to tetrafluorohydrazine.

Later experiments utilized an all-Pyrex apparatus and mercury manometer to follow pressure changes in the system. A covering of halocarbon oil prevented contact of the difluoramine with the mercury. In thoroughly cleaned and dried Pyrex, known Cl-F compounds are stable for short periods.

Difluoramine-Chlorine Trifluoride Systems

In addition to the studies involving the action of pure and uncomplexed ClF_3 and ClF_5 on difluoramine, several other variations in the form of the reactants have been utilized. In particular, $\text{ClF}_2^+ \text{BF}_4^-$, $\text{KF} \cdot \text{KClF}_4$, and RbClF_4 , complexes of ClF_3 , have been used. In some instances an $\text{HNF}_2 \cdot \text{BF}_3$ complex has been employed.

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Neat Reactions. When ClF_3 and HNF_2 were condensed together in a Pyrex reactor and then allowed to warm to melting, an instantaneous reaction was noted by a vapor pressure surge to a constant value. In one instance there was an accompanying audible pop but no flash or light emission. Subsequent fractionation of the volatile materials revealed that all the difluoramine was consumed when equimolar amounts of reagents were used. Some excess HNF_2 over a 1:1 stoichiometry also reacted. Based on the limiting reagent, the yields of ClNF_2 varied from 62 to 95 percent. Smaller amounts of N_2F_4 were produced accompanied by occasional traces of NF_3 . In addition to these N-F moieties, slight but detectable concentrations of ClNO also were found. Although ClF_3 was not recovered, some FClO_2 and ClO_2 were observed. These, together with the ClNO formation, indicated partial hydrolyses: $\text{ClF}_3 + \text{H}_2\text{O} \longrightarrow \text{FClO}_2, \text{HF}$ and $\text{ClNF}_2 + \text{H}_2\text{O} \longrightarrow \text{ClNO}, \text{HF}$. Though the system was initially dry, the action of HF on the Pyrex apparatus would result in O-H formation.

Reactions Involving Complexed Reagents. Because of the rapidity of the $\text{HNF}_2\text{-ClF}_3$ reaction, experiments were carried out using BF_3 as a complexing agent for ClF_3 or HNF_2 . This resulted in the desired moderation of the reaction rate. For example, at -80°C when equimolar amounts of ClF_3 and $\text{HNF}_2\cdot\text{BF}_3$ were mixed, the appearance of ClNF_2 and other N-F species was still noted after 4 days, although most of the total yield was obtained after 40 minutes. This pronounced decrease in the rate of reaction is probably due to the complexing of ClF_3 by BF_3 made available by reaction of HNF_2 , as well as the decrease in free HNF_2 concentration.

Chlorodifluoramine was the principal nitrogen-containing product in these BF_3 systems whether 1:1, 1:2, or 2:1 molar proportions of ClF_3 and HNF_2 were used. The results of these experiments also showed that reaction

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temperatures above -80°C led to an increased proportion of N_2F_4 among the products. The relative amount of N_2F_4 was also increased by an excess of HNF_2 , while the NF_3 yield was increased by an excess of ClF_3 . Nitrogen trifluoride was found only in trace amounts at or below -80°C or when there was no excess of Cl-F reagent.

The solid compounds $\text{KF}\cdot\text{KClF}_4$ and RbClF_4 were treated with pure HNF_2 and it was determined that reaction at -80°C was very slow. The rubidium salt was the least reactive of the Cl-F moieties tested. Definite conclusions regarding the relative reactivity of the potassium salt can be made since in one experiment an explosion occurred upon warming the mixture to room temperature directly from -142°C . However, when the intermediate temperature of -80°C was maintained for some time before further warming, no explosion resulted.

The yields of ClNF_2 obtained with these solid Cl-F compounds were about 50 percent or lower. The larger amounts of N_2F_4 found probably reflect the higher temperatures needed to achieve reaction. The formation of N_2F_4 is increased, then, by increased temperature as well as by the absence of ClF_3 complexing moieties.

The RbF and KF formed or present initially in these reactions proved effective in scavenging the HF obtained during the reactions. To have the greater reactivity of the volatile ClF_3 and yet still eliminate the possible detrimental effects of free HF , some reactions were conducted using NaF to "neutralize" the HF . The results are not yet complete but do not appear to be significantly different than those found in experiments run in the absence of NaF .

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Recovery of Nitrogen-Containing Products. The complete recovery of difluoramine nitrogen as volatile compounds was not realized. The remaining 10 to 20 percent was probably present in a residual white solid. Upon hydrolysis, these solids gave off NO_2 , indicating the presence of NOBF_4 .

This solid did not contain Cl-N-F compounds since all the reactant chlorine was obtained in the volatile materials.

To eliminate the side reactions caused by the glass apparatus, an all-Kel-F and Teflon reactor has been fabricated. Several reactions involving neat ClF_3 and HNF_2 have been conducted in this apparatus to date. For equimolar amounts of ClF_3 and HNF_2 , the results were analogous to those obtained in the glass apparatus, i.e., ClNF_2 was the principal product (59 to 70 percent), with lesser amounts of N_2F_4 and NF_3 being formed. However, all the nitrogen of HNF_2 was recovered as these N-F compounds. Moreover, approximately one-third of the ClF_3 was recovered unreacted. These reactions were run at -80°C . Future work will employ lower temperatures as well as variable mole ratios in the hope of forming and preserving the apparent intermediate F_2NF_2 .

Difluoramine-Chlorine Pentafluoride Systems

Chlorine pentafluoride and difluoramine have been reacted in the metal-Teflon, Pyrex, and Kel-F-Teflon reactors. At present this work has only encompassed the uncomplexed species, but it will be extended to complexed forms. As with chlorine trifluoride, the pentafluoride reacted with difluoramine to give mixtures of ClNF_2 , N_2F_4 , and NF_3 . Unlike ClF_3 , however, a smooth reaction at -80°C gave products which were more sensitive to the

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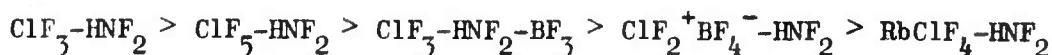


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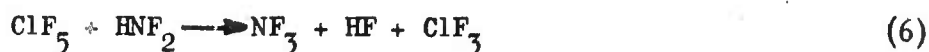
glass environment. Within minutes, the formation of NO_2 could be visibly detected. If not fractionated at once, practically no N-F or Cl-F materials were found. Instead, the degradation products N_2O_4 , HNO_3 , Cl_2 , ClO_2 , and FCIO_3 were obtained. Rapid fractionation of an equimolar reaction mixture yielded as much as 77 percent ClNF_2 with 23-percent recovery of ClF_5 . The remaining HNF_2 was converted to N_2F_4 and NF_3 . In the Kel-F-Teflon reactor, a good correspondence between the amount of ClNF_2 formed and the amount of ClF_5 reacted also was found. The presence of the side products N_2F_4 and NF_3 again indicated a high reactivity of the Cl-F bonds of the original intermediates. Here also, the use of lower temperature was indicated as one means of decreasing this detrimental side reaction.

Factors Affecting Reactivity of Cl-F Bonds

Several significant conclusions are possible despite the failure to prove an exact stoichiometry for the reaction of these Cl-F compounds with HNF_2 . The relative order of reactivity for the various systems was:



The place of $\text{KF}\cdot\text{KClF}_4$ in this series is doubtful but it is probably comparable to that of RbClF_4 . One very encouraging aspect is the fact that the predicted Cl-N bond is established through the interaction of these materials and is stable under these conditions. The alternative possible reactions



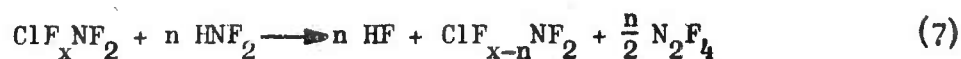
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cannot be occurring to any great extent if at all since no ClF or ClF_3 was observed in the reaction of ClF_3 or ClF_5 , respectively. Very often there was a direct correspondence between the observed amounts of ClNF_2 and the loss of Cl-F species.

Therefore, it appears reasonably certain that the expected ClF_xNF_2 moiety has at least a transient existence. However, the substitution of the NF_2 group into the Cl-F molecule seems to have caused a considerable enhancement in the reactivity of the remaining Cl-F bonds. This gives rise to the side reaction



as well as reactions with the containing medium, in which case degradation may go even further as in the ClF_5 reactions. In fact, warming previously colorless fractions of reaction products in glass has upon occasion resulted in the formation of NO_2 , SiF_4 , and Cl_2 .

Because of this apparent preferential reactivity of the Cl-F fluorines of ClF_xNF_2 with additional HNF_2 , it was decided that an interhalogen fluoride of reduced reactivity should be examined. The compound chosen was IF_5 . The proposed reaction



was examined in both the glass and plastic reactors. Because of the relatively high temperature (0 C) necessary to melt the IF_5 , the reaction was found to give unwanted degradation products, including I_2 . In fact, only small amounts of N-F materials could be found.

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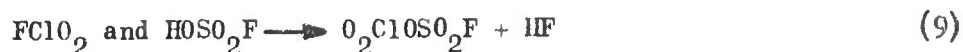
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Difluoramine-Chloryl Fluoride Systems

Another approach designed to establish a Cl-N bond from an active Cl-F compound and HNF_2 involved FClO_2 . This compound has been demonstrated to couple with an acidic hydrogen (Ref. 9):



With HNF_2 , the reaction might be expected to proceed as follows:



This product would not be subject to the degradation reactions of the ClF_xNF_2 molecule since there are no additional Cl-F bonds to react. However, ClO_2 and possibly FClO_2 as contaminants have been credited with deflagrations in previous ClF_3 - HNF_2 experiments (Ref. 10). To facilitate removal of ClO_2 from FClO_2 and at the same time to moderate the reactivity of the FClO_2 , the complex $\text{ClO}_2^+\text{BF}_4^-$ was employed.

Chlorine dioxide was removed from the relatively nonvolatile complex at -80°C . The complex was then transferred to the Kel-F reactor, and HNF_2 was added at -142°C . Upon warming the mixture to -80°C , a deflagration occurred.

The gases, noncondensable at -196°C , came almost exclusively from the HNF_2 . However, among the condensable products, there was a small amount of unidentified material with a sharp doublet infrared absorption at 7.6 and 7.7 microns. This does not correspond to FClO_2 , ClO , or FClO_3 absorptions, and may indicate the desired compound. Unfortunately, the N-F region was obscured by the presence of NF_3 and the sample was too small

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to purify. Nearly all the $\text{FClO}_2\text{-BF}_3$ complex was recovered. It is likely that the deflagration was caused by ClO_2 which was formed during transfer of the complex into the reactor. Experiments in which both the FClO_2 and HNF_2 are complexed with BF_3 have eliminated deflagrations, but the desired compound has not been prepared (the HNF_2 being converted to NOBF_4). Other means of moderating the reaction are being sought. In conjunction with the continued use of HNF_2 as a means of introducing the NF_2 group into Cl-F moieties, efforts will be extended to include other reactions of $\text{NF}_2\cdot$ and $:\text{NF}$ radicals.

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EXPERIMENTAL DETAILS

PREPARATION OF MATERIALS

Halogen Fluorides

Chlorine trifluoride was prepared from $\text{KF} \cdot \text{KClF}_4$ as described previously (Ref. 1) and was also obtained from the Rocketdyne pilot plant production of ClF_5 , contaminated in this case with 2 to 3 percent ClF_5 but no Cl-O compounds. ClF_5 from the Rocketdyne pilot plant (99+ percent purity) was used directly.

Iodine pentafluoride was transferred from a lecture bottle to a Teflon trap on the metal vacuum line. By pumping on the discolored solid as it warmed from -196°C , the colored impurities could be removed. The remaining IF_5 was found to be pure by infrared analysis.

Chloryl fluoride mixed with chlorine dioxide was formed from ClF_3 and KClO_3 . The ClF_3 was condensed into a stainless-steel bomb containing KClO_3 and allowed to stand at room temperature overnight. Addition of BF_3 to this mixture at -80°C gave the white solid $\text{ClO}_2^+ \text{BF}_4^-$ from which the uncomplexed ClO_2 was pumped off.

Preparation of Ozone

Oxygen was partially condensed at -196°C and then allowed to pass through an electrodeless discharge zone into another -196°C trap by removing the liquid nitrogen from the first dewar flask and quickly replacing the cold

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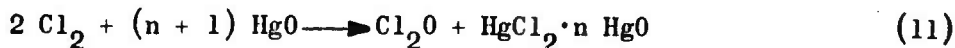


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flask. An intentionally inefficient voltage was used to give a 3-percent conversion to O_3 at 160 mm Hg. After pumping off the unconverted oxygen, conveniently small amounts of pure ozone remained. Several runs were shown to give reproducible quantities by measuring the O_3 pressure by means of a small manometer. Thereafter the ozone was condensed, without first expanding, into a Kel-F infrared gas cell fitted with AgCl windows, for further reaction.

Preparation of Cl_2O

Chlorine monoxide was prepared fresh and in high purity from the reaction of chlorine gas diluted with nitrogen and dry yellow mercuric oxide (Ref. 11).



The Cl_2O was stored in Pyrex ampoules at $-196^\circ C$.

Tetrafluorochlorine (III) Salts

The salts, $RbClF_4$ and $KF \cdot KClF_4$, were made from ClF_3 and the appropriate alkali fluoride (Ref. 12). The $RbClF_4$ was a slightly crystalline white solid, while the $KF \cdot KClF_4$ was an off-white powder.

Alkali Metal Fluorides

To ensure dry potassium fluoride and cesium fluoride, both compounds were first fused and then powdered and handled in a dry box.

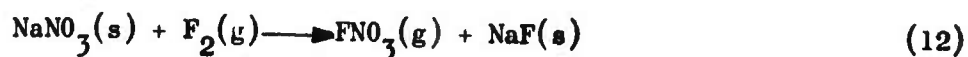
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Preparation of Fluorine Nitrate

Fluorine nitrate was prepared by the reaction of F_2 on dried $NaNO_3$ (Ref. 13).



The FNO_3 was stored at ambient temperature in a stainless-steel cylinder.

Preparation of HNF_2

Diffluoramine was prepared by the aqueous fluorination of urea followed by the treatment of the fluorinated urea solution with concentrated H_2SO_4 . The impure HNF_2 was purified by low-temperature fractionation and was stored in glass ampoules at ambient temperature.

During the purification of one batch of impure HNF_2 , the extreme sensitivity of difluoramine was again demonstrated by a violent explosion destroying a portion of the glass vacuum system.

REACTIONS

Reaction of FNO_3 and HNF_2

Approximately 10 grams of dried KF were placed in the bottom of a Kel-F ampoule using a dry box. The ampoule was transferred to a glass vacuum system where 27.4 cc of HNF_2 were condensed over the KF. The ampoule

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was warmed from -142 to -80 C to ensure contact of the HNF_2 with the KF . The ampoule was recooled to -142 C, and the FNO_3 (20.7 cc) was condensed over the KF-HNF_2 . The ampoule was slowly warmed to -80 C and kept at this temperature for 42 hours. The reaction products were fractionated using the metal vacuum system and examined by infrared analysis.

Fluorination Reactions

Fluorinations were carried out using a 300-milliliter stainless-steel, high-pressure Hoke cylinder fitted with a high-pressure Hoke needle valve (Y3002H). The Cl_2O was condensed into the cylinder from a metal high-vacuum system. The desired amount of fluorine was then condensed into the cylinder at -196 C. The cylinder was then warmed to the desired reaction temperature. Solid starting material was handled in the dry box. Fractionation of the products was carried out in a metal vacuum system equipped with Teflon traps. Identification of reaction products was by infrared analysis using an infrared cell constructed of stainless steel and equipped with AgCl windows.

Reactions With HNF_2

The reactions of difluoramine and the halogen fluorides were performed by the following procedure. The least volatile compound of the pair was first condensed in the bottom part of the apparatus; the more volatile or lower-melting compound, usually HNF_2 , was condensed above the other material. Changing the cooling baths after closing the system allowed the upper compound to melt and run down as a liquid into the second reactant.

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In this manner, mixing was generally attained in the liquid state as well as in the vapor state. After selected reaction times at a particular temperature, fractionation under vacuum began. This was usually done without pumping so that the product NF_3 would not be lost, and was facilitated by the absence of any -196°C noncondensable gases in nearly all reactions.

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